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Internal rotation in 1,2-di-(p-XC_6H_4)ethanes (X = H, Br, NO_2): infrared spectra and compensation effect

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Abstract

Infrared absorption spectra and internal rotation of 1,2-di-(p-XC_6H_4)ethanes (X = H, Br, NO_2) in crystalline phase, liquid and solutions at various temperatures have been investigated. Band fitting was applied to conformationally sensitive regions of the spectra, and assignment of the peaks to *trans* and *gauche* conformations was performed. Enthalpy and entropy differences of the conformers (ΔH_0 and ΔS_0) were found to be solvent-dependent, and it is interpreted in terms of previously discovered compensation effect. The values ΔH_0 and ΔS_0 for 1,2-di-(p-$NO_2C_6H_4$)ethane obtained are unusually large.

Keywords: Infrared spectra; Molecular dynamics; Conformational equilibrium; Compensation effect

1. Introduction

Internal dynamics of molecules is of great interest because it affects important physical and chemical properties of fluids and solids. In addition, internal rotation in molecules was successfully utilised as probe of intermolecular interactions in liquids and local molecular dynamics in glassy polymers (method of conformational probes [1]). Earlier a compensation effect in thermodynamics of conformational equilibria of various small molecules was discovered [2–4]. The goal of the present work is to study conformational equilibria in molecules with relatively large sizes of their mobile groups. In this paper we describe vibrational spectra and the molecular dynamics of 1,2-di-(p-nitrophenyl)ethane (DPNPE) and 1,2-diphenylethane (DPE). Earlier we have studied the infrared spectra and the internal rotation of 1,2-di-(p-bromophenyl)ethane (DPBPE) [5] and have used DPBPE as a probe [6]. The use of DPNPE and DPE as probes is perspective, and for that it is necessary to obtain information about their vibrational spectra and thermodynamic parameters of conformational equilibria. The series of selected molecules provides a possibility to investigate the influence of p-

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